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Fabrication of Three-Dimensional Tyranno Fibre Reinforced SiC Composite by the Polymer Precursor Method

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Abstract: A three-dimensional Tyranno fibre reinforced SiC composite was fabricated by infiltration of molten polycarbosilane into three-dimensional textile preform (volume fraction; 39%) in an autoclave followed by pyrolysis in argon up to 1200°C. An attempt to improve the density of the composite was done by repeated infiltration and pyrolysis. As a result of 10 times repetition, the density of the composite was increased to 2.4 g cm^{-3} (relative density; 83%, open porosity; 5%). Bending strength and fracture toughness were 420 MPa and 11.5 MPa $m^{1/2}$, respectively. The composite showed semistable fracture behaviour because of bridging of fibre parallel with the tensile direction. © 1998 Elsevier Science Limited and Techna S.r.l. All rights reserved

1 INTRODUCTION

Advanced ceramics are in general outstanding for their thermal and oxidation resistance, and strength. Fracture toughness of ceramics is intrinsically low, and research is in progress to improve their toughness and reliability. Ceramic composite materials are being intensively developed for their reliable use in oxidising atmosphere at high temperature. Continuous fibre reinforced ceramic composites are felt most promising for their non-catastrophic failure mechanisms.

Continuous fibre reinforced composites are classified into one-dimensional, 2-D, and 3-D reinforced from a point of view of fibre orientation. 1-D and 2-D can be fabricated by hot-pressing to obtain sufficiently dense composites although they suffer for delamination. On the other hand, 3-D composites do not have problem of delamination, possess high shock resistance, capability of complicated shape, and easiness of basic design by orientation and volume fraction of fibre. This is the reason why 3-D fibre reinforced composites have been studied intensively in recent years.[1,2]

Three-dimensional reinforced composites, however, cannot be fabricated by pressure processes such as hot-pressing. This means that it is difficult to make dense 3-D reinforced composites, unless the infiltration methods such as the polymer precursor method[1,3–6] and reaction bonding[7] (liquid phase infiltration), chemical vapour infiltration[1] (gas phase), and slip infiltration[2] (solid phase) are used. Among these the polymer precursor method makes it possible to obtain dense composite by repetition of the infiltration and pyrolysis process which is relatively simple although time consuming.

In this work, 3-D Tyranno fibre reinforced SiC composites were fabricated by infiltration into a 3-D textile preform followed by pyrolysis of polycarbosilane (PCS). The mechanical properties of the composites also have been studied.

2 EXPERIMENTAL

2.1 Materials

In this work LoxM grade of the continuous Si–Ti–C–O Tyranno fibre (UBE Industries Ltd, Japan) has been used. Density, filament, and sizing agent

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of this fibre were 2.37 g cm^{-3}, 1600 $yarn^{-1}$, and polyethylene oxide, respectively. Diameter of the fibre was 8.5 μm in x and y directions and 11 μm in z direction. This fibre was woven to right-angled 50×25×5 mm 3-D preform. The volume fraction of fibre was 39%. No operation for removing sizing agent prior to the infiltration process was done.

PCS (Nippon Carbon Co., Ltd, Japan), the precursor of NICALON fibre, used in this work was lot number 9C-07, whose density, molecular weight, and melting point were 1.12 g cm^{-3}, 1335 (number average), 2793 (weight average), and 239°C, respectively.

2.2 Fabrication process

The fabrication process of the composite used is shown in Fig. 1. PCS was infiltrated into 3-D preform in an autoclave at 300°C for 1 h under 10 MPa argon pressure. PCS-fibre composite obtained by the infiltration process was put out from solidified PCS, and then pyrolyzed in a 0.1 MPa argon atmosphere up to 1200°C at heating rate of 1°C min^{-1} from room temperature to 300°C, 0.1°C min^{-1} from 300 to 500°C, and 1°C min^{-1} from 500 to 1200°C. This infiltration–pyrolysis process was repeated 10 times to obtain dense composite.

2.3 Characterization

Density and open porosity of the composite at each step of densification were measured by the liquid displacement method based on JIS R-2205. Three-point bending strength of the composite at room temperature, 1000, and 1200°C in air was measured with crosshead speed of 0.5 mm min^{-1}, and span of 30 mm based on JIS R-1601 and 1604. Fracture toughness was measured by the single edge notched beam (SENB) method, on 3 mm width ×4 mm height samples with a straight notch of 1.5 mm depth. Span was 30 mm, and crosshead speed was 0.5 mm min^{-1}. The work of fracture of the composite was calculated from the area of load–cross head displacement chart in bending strength test and fracture toughness test. Fractured sample in bending test was observed by scanning electron microscopy (SEM) and optical microscopy.

3 RESULTS AND DISCUSSION

3.1 Density and open porosity

Figure 2 shows density and open porosity of the composite. Density of the composite was increased to 2.4 g cm^{-3} (relative density; 83%) by 10 times repetition of infiltration–pyrolysis process. The effect of infiltration on density of the composite went down gradually with the progress in infiltration because of decreasing open porosity. After 10 infiltrations, the composite open porosity was of only 5% but also closed large pores were observed between fibre yarns during composite polishing. This is the reason for the relative density of the

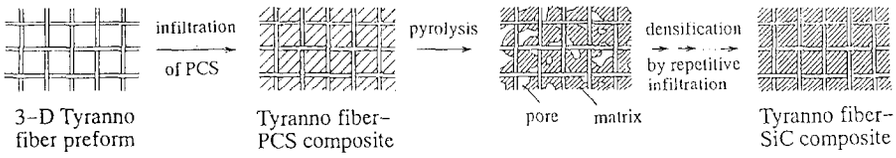

Fig. 1. Process for fabricating 3-D Tyranno fibre reinforced SiC composite.

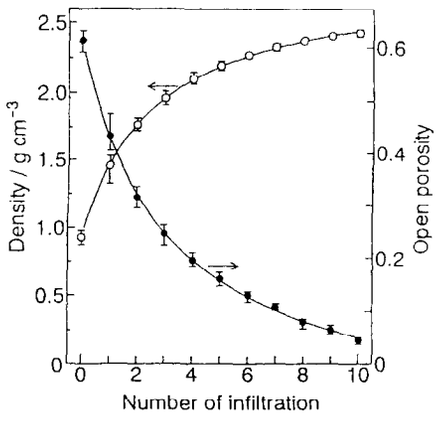

Fig. 2. Density and open porosity of the composite.

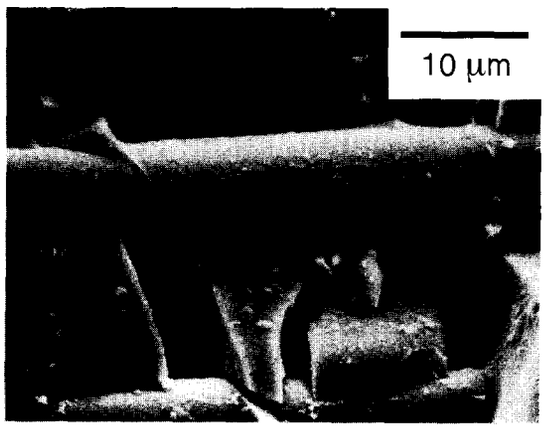

Fig. 3. SEM micrograph of the composite by 1 infiltration.

composite by 10 times infiltration being of only 83% in spite of open porosity of only 5%.

Figure 3 is an SEM micrograph of the composite after only 1 infiltration, showing a satisfactory bonding between PCS produced matrix and fibre. That is the reason why density of the composite was rather improved though it was very difficult to obtain sufficiently dense materials in the case of SiC–SiC whisker composites,[3,4] where the maximum density attained was only *ca.* 62%. It might be difficult, however, to obtain denser composite by the process used in this work because of volume shrinking of matrix and gas generation in the pyrolysis process, which might cause closed pores in the composite.

3.2 Bending strength

Figures 4 and 5 show room temperature bending strength and load–crosshead displacement curves, respectively, for the composite. Bending strength was remarkably improved to 420 MPa with the increase in density by 10 times infiltration. No test sample completely fractured off to two pieces in bending test because fibre yarns in a crosshead side were not cut off. As shown in Fig. 5, this composite showed semistable fracture behaviour, especially in the case of the one subjected to 5 times infiltration. Figure 6 shows an optical micrograph of fractured sample fabricated by 10 times infiltration in bending test. Bridging of fibre parallel with the tensile direction which was cut off in various places near the fractured surface is clearly observed, which is suggested as the main factor for the semistable fracture behaviour of this composite, leading to non-catastrophic failure.

Figures 7 and 8 show bending strength at 1000 and 1200°C for the composite obtained by 10 times infiltration and the relative load–crosshead displacement graphs. The composite still had bending strength of 300 MPa and semistable fracture behaviour even at 1200°C. Figure 9 shows optical micrographs of fractured sample in high temperature bending test. The crack propagates in a rather straight manner from a microscopic viewpoint and fibre bridging considerably decreased compared to the room temperature test. It has been argued that the deterioration of bending strength of the composite at high temperature is caused by the drop of strength of fibre itself at high temperature and by matrix and/or fibre oxidation for the high temperature bending test being carried out in air.

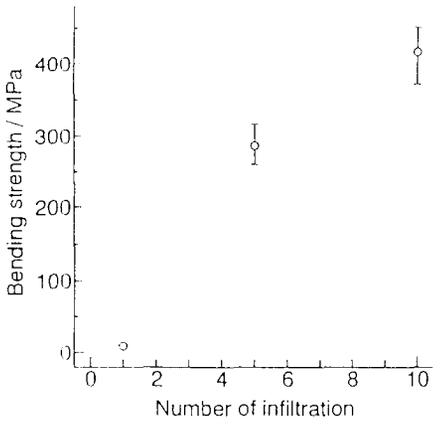

Fig. 4. Bending strength at room temperature of the composite.

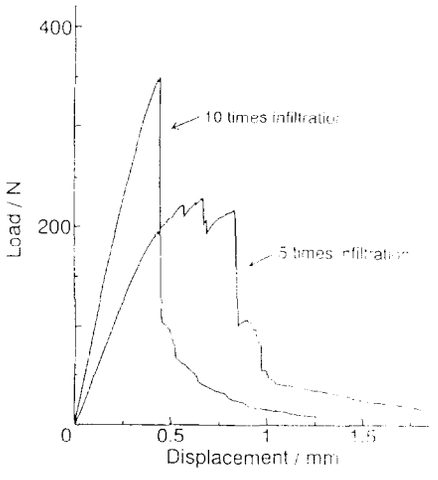

Fig. 5. Load crosshead displacement graphs in bending test.

Fig. 6. Optical micrograph of fractured sample fabricated by 10 times infiltration in bending test.

3.3 Fracture toughness and work of fracture

Figure 10 shows the fracture toughness of the composite measured by the SENB method. The composite had very high fracture toughness values of 11.5 and 7.1 MPa $m^{1/2}$ by 10 and 5 times infiltration, respectively, which are considerably higher than for ordinary monolithic SiC sintered body; 2–3 MPa $m^{1/2}$. High fracture toughness values had been also expected from the semistable fracture behaviour of the composite. Figures 11 and 12 show the work of fracture of the composite; open circles mean work of fracture in bending test and filled circles mean work of fracture obtained from toughness measurement. The fracture energy of the composite was 2 orders of magnitude higher than for ordinary monolithic SiC (typically 11–83 J m^{-2}).[8] It was argued that the large work of fracture of the composite resulted from the remarkable fibre pull-out, as shown in Fig. 13. A combination of significant fracture and high fracture toughness means good reliability of the material and its prospective reliable use for structural applications.

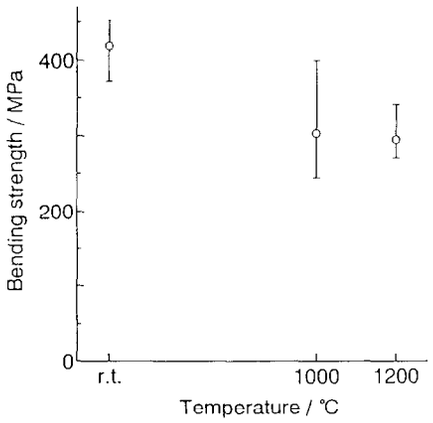

Fig. 7. Bending strength of the composite by 10 times infiltration.

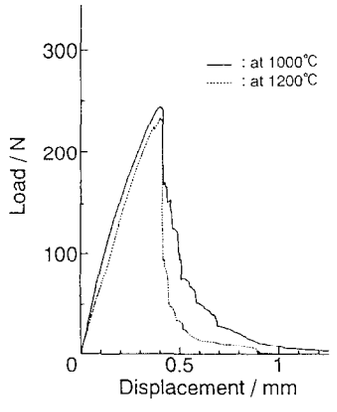

Fig. 8. Load–crosshead displacement graphs in high temperature bending test.

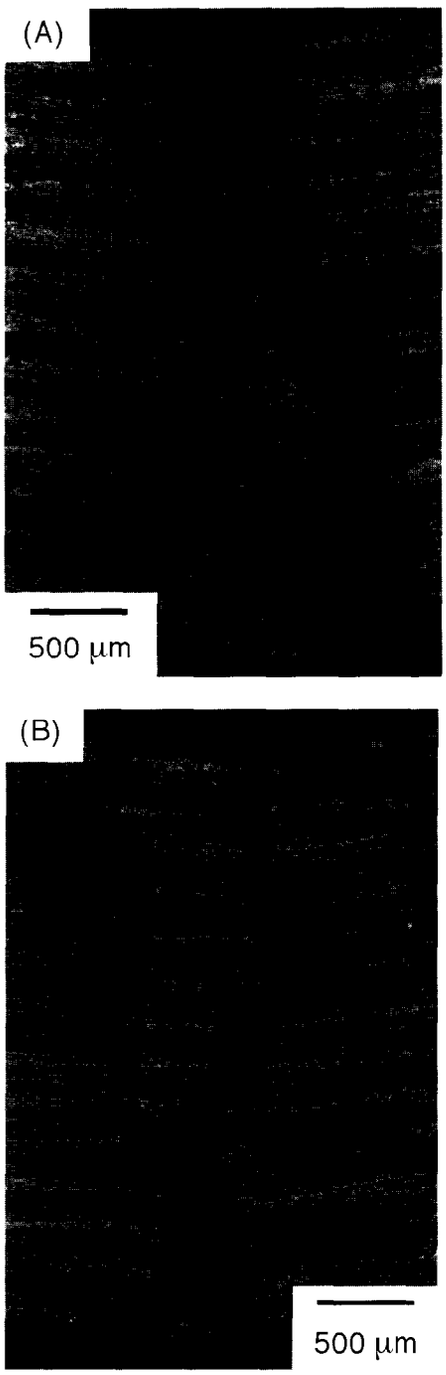

Fig. 9. Optical micrograph of fractured sample fabricated by 10 times infiltration subjected to high temperature bending test; at 1000°C, (A) and at 1200°C, (B).

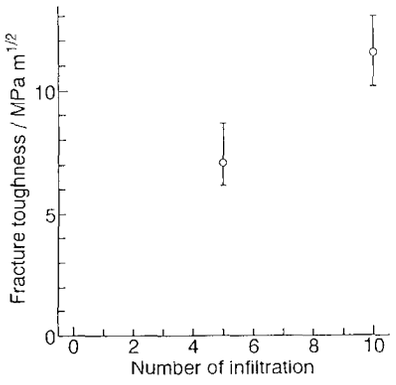

Fig. 10. Fracture toughness of the composite.

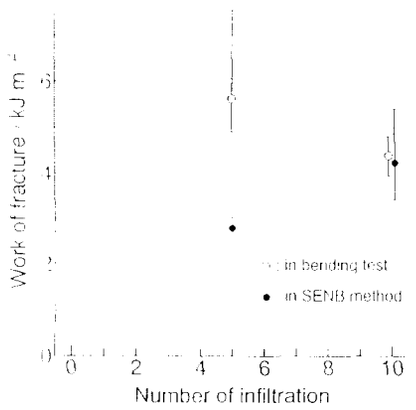

Fig. 11. Work of fracture of the composite; open circles mean work of fracture in bending test and filled circles mean work of fracture by toughness measurement.

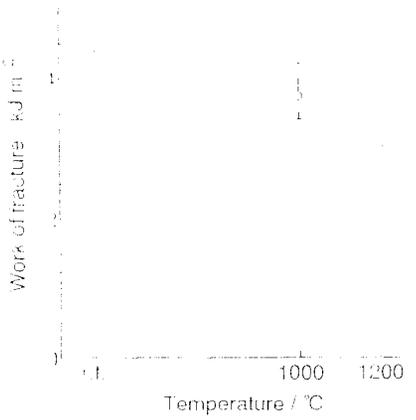

Fig. 12. Work of fracture of the composite by 10 times infiltration in bending test.

Figure 13 shows a room temperature SEM micrograph of a fractured surface of the 10 times infiltrated composite. Remarkable fibre pull-out can be observed, this contributing high fracture toughness and large work of fracture to the composite. Nevertheless, fibre pull-out was not so remarkable at high temperature as is shown in Fig. 14. It can therefore be inferred that the fracture toughness at high temperature of the composite,

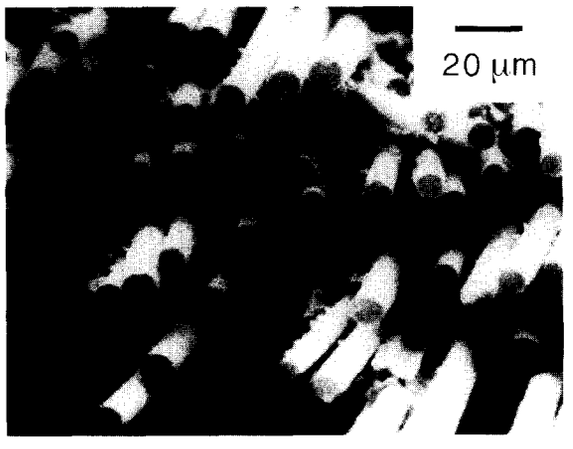

Fig. 13. SEM micrograph of a fractured surface of the composite by 10 times infiltration fractured at room temperature.

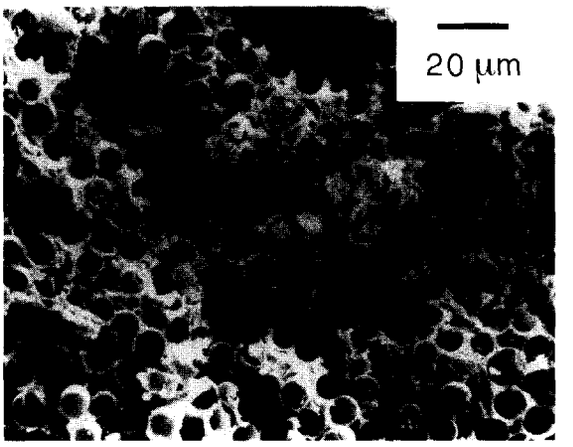

Fig. 14. SEM micrograph of fractured surface of the composite by 10 times infiltration fractured at 1200°C.

which had not been measured, might be lower than for the one obtained at room temperature. In fact bending strength and work of fracture at high temperature were lower than those at room temperature and fibre pull-out at high temperature was also shorter.

4 CONCLUSION

1. A three-dimensional Tyranno fibre reinforced SiC composite was fabricated by infiltration of molten PCS into three-dimensional textile preform followed by pyrolysis.
2. A composite with a density of 2.4 g cm^{-3} (relative density; 83%, open porosity; 5%) was obtained by 10 times repetition of the infiltration and pyrolysis process.
3. The composite had bending strength of 420 and 300 MPa at room temperature and at 1200°C, respectively. Fracture toughness of the composite was 11.5 MPa $m^{1/2}$, and work of fracture was 4.3 kJ m^{-2}. Both were considerably superior to those of ordinary monolithic SiC.
4. The composite showed semistable fracture behaviour to avoid catastrophic fracture because of bridging of fibre parallel to the tensile direction.

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